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PROTECTIVE LAYER FOR AN ALUMINUM-CONTAINING ALLOY FOR HIGH-
TEMPERATURE USE AND METHOD OF PRODUCING SUCH A PROTECTIVE LAYER

The invention relates to a protective layer for an
aluminum-containing alloy for high-temperature use, in particular at
5 temperatures up to 1400°C. The invention further relates to a
method of producing such a protective layer on aluminum-containing
alloys.

Prior art

Alloys based on Fe-Al, Ni-Al, Ni-Cr-Al or Fe-Cr-Al are
10 characterized by an excellent oxidation resistance at very high
operating temperatures ($\approx 1400^\circ\text{C}$). Alloys based on Fe-Al, Ni-Al,
Ni-Cr-Al or Fe-Cr-Al are characterized by excellent oxidation
resistance at very high operating temperatures ($\approx 1400^\circ\text{C}$). This
resistance is due to the formation of a thick and slowly growing
15 aluminum oxide layer, which forms with high temperature application
on work surfaces (alloys). This protective cover layer, which is
caused by selective oxidation of the alloying element aluminum,
only occurs, when the aluminum content in the alloy is sufficiently
large, e.g., at least about 8% by weight in Fe-Al or Ni-Al alloys,
20 and at least about 3% by weight in Fe-Cr-Al or Ni-Cr-Al alloys.

Due to the formation of the cover layer of aluminum
oxide, the alloying element present in the aluminum alloy is used
up. The use per time unit is generally proportional to the oxide
growth rate, and thus increases with increasing temperature, since
25 the oxide growth rate (k in cm^2 per second) increases with
increasing temperature. The aluminum reservoir present as a whole

in an aluminum-containing alloy increases proportionally with the wall thickness of a relevant component. When the component is a layer or foil, the strength typically is proportional to the thickness of the layer, and when the component is a wire, for example to the diameter.

If due to long-term application of a component consisting of an aluminum-containing alloy and the formation of an aluminum oxide layer on its surface, the aluminum content of the alloy is reduced to such an extent that it falls below a critical aluminum concentration, then a further protecting aluminum oxide layer can no longer form. This results in very quick "breakaway oxidation." This time matches the so-called end of life of the components.

It follows from the above considerations that the life of a component declines either with increasing oxide growth rate or decreasing wall thickness.

Some examples of typical remaining-life times (t_B) of components consisting of FeCrAl alloys (commercial names, e.g., KANHAL AF or ALUCHROM YHF) varying with the temperature and wall thickness are known from the literature. For instance,

for a 1 mm wall thickness at 1200°C, about 10,000 h,
for a 0.05 mm wall thickness at 1100°C, about 700 h,
for a 0.05 mm wall thickness at 1200°C, about 80 h.

Theoretical considerations allow the inference that with a 100°C temperature increase, the life span decreases by about a factor of 10. The t_B temperature dependence follows from the known temperature dependence of the oxide growth rate k , which is defined as follows:

$$k = k_0 e^{-Q/RT}$$

where Q = the activation energy for diffusion processes in the layer, T = temperature, and R = general gas constant. The remaining-life time (t_b) dependence of the component wall strength (d) can be stated for most applications approximately like this:

t_b proportional to d^3 .

This illustrates the strong reduction of the remaining-life time, when component wall strength is reduced. For very thin-walled components consisting of the above-mentioned alloys, as are present, e.g. in car-catalyst substrates (foil thicknesses 0.02 to 0.1 mm), in fiber-based gas burners, or filters (fiber diameter 0.015 to 0.1 mm), operating times of a few thousand hours as are required in practice are only possible if the operating temperatures are kept relatively low, e.g. around 900°C.

However, in this temperature range, especially between 800 and 950°C, the growth rate (k) of the oxide layer disadvantageously exhibits a distinct variance from the above-mentioned temperature dependence. This difference occurs especially in the initial stage (e.g. up to approximately 100 h) of oxidation stress. This variance is due to the fact that at temperatures about 800°C, the α - Al_2O_3 formed at high temperatures (at and above 1000°C) (hexagonal structure; corundum lattice) does not occur, whereas metastable Al_2O_3 modifications, especially θ - or γ - Al_2O_3 , do. These oxide modifications are characterized by significantly higher growth rates than has α - Al_2O_3 . They generally occur only in the initial stages of oxidation. After long periods,

transition to stable α -Al₂O₃ with corresponding low growth rates occur.

The life span of a component at 900°C therefore cannot generally be extrapolated from the oxide growth rates known at higher temperatures. For thick-walled components with a wall thickness of 1 to 2 mm, for example, this is generally not a problem, since the aluminum reservoir in the alloy is sufficiently high that the initial high growth rate at temperatures around 900°C, due to the metastable oxide modifications, does not result in a significant reduction of the total aluminum reservoir.

However, for very thin components, e.g. 0.003 to 0.1 mm thin foils, because of the initial high growth rate of the oxide layer, the existing very small aluminum reservoir may be exhausted disadvantageously even within a few hours. This regularly causes complete destruction of the components. The actual life span is therefore less by orders of magnitudes, as could be expected from the extrapolation of the growth rates of the α -Al₂O₃ layers at high temperatures (1000 to 1200°C). The above-mentioned alloys are therefore not suitable for application in the afore-mentioned thin-walled components, e.g. car catalysts, gas burners or filter systems.

Object and solution

The object of the invention is to provide a method, whereby aluminum-containing alloys form an oxide cover layer substantially composed of α -Al₂O₃ when applying a temperature exceeding 800°C, especially in the initial phase of oxidation, thereby exhibiting clearly improved long-term behavior.

The problem of the invention is solved by a method for treating aluminum-containing alloys for high-temperature use according to the main claim. Advantageous embodiments of the method are disclosed in the dependent claims.

Subject of the invention

Within the scope of the invention, it was found that surface treatment of aluminum-exhibiting alloys based on Fe-Al-, Ni-Al, Ni-Cr-Al and Fe-Cr-Al causes improved long-term stability, when using these alloys at temperatures, at which metastable Al_2O_3 modifications appear. This surface treatment advantageously causes regular inhibition of the formation of metastable Al-oxides under subsequent operational application at higher temperatures around 900°C , especially in the temperature range of 800 to 950°C .

The process according to the invention is based on the fact that the presence of other, i.e. non-aluminum-containing oxides on the surface of an aluminum-containing alloy, or a similar component, promotes the formation of the advantageous $\alpha\text{-Al}_2\text{O}_3$ at operating temperatures above 800°C . Thus, the disadvantageous formation of metastable Al_2O_3 modifications, such as $\theta\text{-Al}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$, is suppressed, whereby the non-aluminum-containing oxides act on the surface of the alloy as nucleating agents promoting especially the formation of the $\alpha\text{-Al}_2\text{O}_3$ modification at temperatures above 800°C . This effect occurs advantageously right at the beginning of the oxidation of the alloy and at operating temperatures, thus regularly preventing the harmful formation of metastable aluminum oxides from the start.

Useful examples of such oxides acting advantageously on the surface are especially Ni oxides, Fe oxides, Cr oxides and Ti oxides. The oxides may be deposited on the surfaces of the components consisting of the said metallic, aluminum-containing alloys or also created by various methods.

These include, especially

Direct deposition of the aforesaid oxides on the alloy surface, e.g. through vaporization and condensing, or cathode sputtering.

Direct deposition of a metallic layer consisting of Ti, Cr, Ni or Fe on the surface of an alloy using deposition methods known from prior art. With a high-temperature application of above 800°C, the said metals convert to the desired oxides in an oxygen atmosphere.

Treatment of the alloy in a chloride- and/or fluoride-containing solution, or a gaseous atmosphere, in which such a solution is present. A Fe-, Ni- or Cr-containing oxide or hydroxide thus forms at the surface of the alloy, depending on the alloy base. With a high-temperature application, the hydroxides convert to their corresponding oxides.

A temperature treatment of the alloy, whereby a temperature below 800°C is initially set, [and] whereby preferably the additional alloy elements (except aluminum) form an oxide layer on the surface.

All these methods have in common that initially an oxide layer, which does not substantially consist of an aluminum oxide, forms on the surface of the alloy. Moreover, to get the desired effect of the advantageous formation of an α -Al₂O₃ layer, or the inhibition of metastable aluminum-oxide layers, it may be sufficient when the surface layer exhibits further, non-aluminum-containing oxides with a concentration of at least 20%, and especially above 50%.

By a surface layer of the alloy is meant a near-surface area with a thickness of up to 1000 nm. Within the scope of the invention, it has emerged that the action of the non-aluminum-containing oxides on the surface of the alloy already occurs with a thickness of the layers of only a few nm.

Special specification section

The subject of the invention will be explained in more detail in reference to a figure and several examples, without limiting the scope of the invention.

A schematic representation of the dependence on temperature of the oxide growth on alloys of the Fe-Al, Fe-Cr-Al, Mi-Al or Ni-Cr-Al type is provided in the figure.

The dashed lines indicate the thickness of an oxide layer formed on the surface of a corresponding alloy with exclusive formation of α -Al₂O₃ at the corresponding temperatures versus time (both in arbitrary units). After an initial somewhat steeper gradient of the growth rate, it then remains almost constant causing an almost linear increase of the thickness of the layer

over longer periods. Altogether, the formed thickness of the layer increases, when the relevant operating temperature decreases.

Moreover, for a temperature of 900°C, indicated by a continuous line, the thickness of the layer at the initial formation of metastable aluminum oxides and subsequent formation of α -Al₂O₃ is indicated. The comparison highlights the distinctly higher growth rate of the metastable aluminum oxides, precisely in the initial stage. During the further process, the growth rate remains almost constant, so that over time, an almost linearly increasing thickness of the layer forms.

As treatment methods for obtaining the advantageous non-aluminum-containing oxides on the surface of aluminum-containing alloys, the methods described in the following have proven especially effective:

1. A Ni oxide, Fe oxide, Cr oxide or Ti oxide is deposited during vaporization and condensation on the surface of a component consisting of an aluminum-containing alloy with a preferred thickness of 5 to 1000 nm. This deposition method is thus equivalent to the prior art.

2. On the surface of a component consisting of an aluminum-containing alloy, a metallic layer consisting of Fe, Ni, Cr or Ti is initially deposited to get a thickness of 5 to 1000 nm by common deposition methods. As suitable deposition methods, especially vaporization and condensing, cathode sputtering, galvanic coating may be mentioned. For operational application, i.e. at temperatures above 800°C, these metals convert to the corresponding oxides in an oxygen atmosphere.

3. A component consisting of an aluminum-containing alloy is treated in a chloride- and/or fluoride-containing solution, or in a gaseous atmosphere, in which such a solution is present. A suitable solution is, for example, a 10% NaCl solution in water. This treatment is done at room temperature, or at a slightly increased temperature of about 80°C. During this treatment, which is done over a period of a few minutes and up to two hours, a Fe- or Ni-containing oxide and/or hydroxide forms at the surface of the component, depending on the alloy base. With subsequent high-temperature application, the possibly present hydroxide converts to the desired Fe oxide (Fe_2O_3) or Ni oxide (NiO).

4. A component is initially exposed to a temperature of 750°C for a period of a few minutes up to five hours, whereby a Fe- or Ni-containing oxide forms on the surface depending on the alloy base.